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Encapsulated neem extract containing Azadiractin-A *within* hydrolyzed poly(vinyl acetate) for controlling its release and photodegradation stability

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ABSTRACT

Neem extract containing Azadiractin-A (neem Aza-A), encased in microcapsules, in a matrix of partially hydrolyzed poly(vinyl acetate) crosslinked with glutaralaldehyde 5% (w/v) and 0.05% hydrochloric acid was prepared via a spray drying technique. The photostabilization of unencapsulated and encapsulated neem Aza-A when exposed to ultraviolet light was evaluated. Neem Aza-A solutions and neem Aza-A microcapsules were applied onto the surface of glass slides. At particular intervals, the remaining concentration of neem Aza-A was measured by HPLC. When the ratio of 87% hydrolyzed poly(vinyl acetate) to water was 1:40 this produced the highest concentration of neem Aza-A after exposure to UV. The degree of swelling ratio of microcapsule depended on the crosslinking density and the crystalline content. The neem Aza-A release was measured in water at 25 °C and the effects of different matrices and other parameters such as polymer–water ratios and particle size were studied. The release mechanism of the neem Aza-A from the microspheres was also investigated.

1. Introduction

The use of conventional broad-spectrum synthetic insecticides is in decline due to public concern and regulatory demands for the use of selective and environmentally benign pest control products. Consequently, in recent years, research has been increasingly focused on the development of natural insecticides originating from plants, because it is believed that they are innocuous. Currently, some attention is being given to the use of neem-based botanical insecticides [1,2]. Neem (Azadiractin indica A.Juss.) is a tree belonging to the Meliaceae family and is widely distributed in South Asia, South-East Asia, and some other tropical areas [1,2]. The major insecticide from neem seed kernels is the tetranortriterpinoid, Azadiractin-A (Aza-A). Aza-A, is a powerful deterrent to insect feeding and a growth-regulating substance, that shows considerable promise as an insecticide [3]. It can suppress at least 200 species of insect pests belonging to different orders, associated with agriculture and storage, causes negligible hazard to nontarget organisms including humans but it has a short environmental persistence [2]. Its short environmental persistence is due to the presence of sensitive moieties such as p-electrons, ester linkages, and an epoxide ring [3]. However, the major problem is its sensitivity to photodegradation so it is rapidly lost in sunlight. This limits its use in agriculture because an insecticide should persist long enough to cause the death of the insect pest. Many researchers have attempted to stabilize Aza-A. Microencapsulation has been used to try to solve this problem. Microencapsulation encloses the sensitive ingredients within a coating or wall material [4]. The wall material protects the sensitive ingredient (or core) against adverse reactions, prevents the loss of volatile ingredients, and can control the rate of release of the ingredient. Wei-Hong and co-worker [3] reported that mixing Aza-A with UV light absorbers can enhance its photostability. The addition of ferulic acid, gallic acid, and rutin provided a moderate degree of photostabilization of Aza-A. In addition, numerous investigators have concentrated on the encapsulation of neem into urea formaldehyde crosslinked starch (UF-St), guar gum (UF-GG) and UF-(St + GG) [5,6], lipophilic substances [7], and sodium alginate (Na-Alg) [8]. In this work, neem had been encapsulated in partially hydrolyzed poly(vinyl acetate) (or poly(vinyl alcohol)) by spray drying. Here, we report on the effect of glutaraldehyde crosslinked poly(vinyl alcohol) type with 0, 40 and 87% hydrolysed poly(vinyl acetate) on the efficiency of encapsulating neem Aza-A. This is the first report on the quality of capsules of neem Aza A encapsulated in glutaraldehyde crosslinked poly(vinyl alcohol). In addition, this is the first report of the photodegradation of neem Aza A in capsules obtained using different percentage hydrolysed poly(vinyl acetate) types. Poly(vinyl alcohol) has been used as a polymer matrix for encapsulation of the reactive agents [9–12] because it is a biodegradable polymer and cheap to make. Spray drying is used for producing pharmaceutical powders for inhalation,

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etc. [13–19]. The production method has a major effect on the physical properties of the capsules such as flowability, hygroscopicity and dissolution. Variations in the production methods cause variations of the physical state (amorphous versus crystalline), particle size and composition at the particle surface. In addition, the biological activity of compounds enclosed in the particles is influenced by the drying process. In some particular cases of spray drying, several impose stresses that can destabilize proteins and peptides, such as high pressure, high shear and immense air–liquid interfaces during atomisation, heating and dehydration [16]. In the process, the sensitive ingredient is mixed or homogenized in a solution containing wall material in which it forms a stable emulsion. The emulsion is then fed into a spray dryer where it is converted to a dried particle. However, spray drying provides the possibility of creating particles with the active protein in one step, which are then suitable for inhalation [16]. To the best of our knowledge, this study is the first of its kind in which the partially hydrolysed poly(vinyl acetate) beads containing neem Aza-A are prepared by the spray drying technique. In the work presented here we test the feasibility of encapsulating neem Aza-A in a matrix made from poly(vinyl alcohol) to produce a product with good end-use properties. The efficiency of encapsulating neem Aza-A were also studied. The photodegradation and release of neem Aza-A in the capsules was also evaluated.

2. Materials and methods

2.1. Materials

Neem seed kernels were purchased locally in Thailand; Aza-A extract was prepared according to the procedure given in Section 2.2 below. Polymers used in this experiment were (1) poly(vinyl alcohol) (PVA) (Fluka) with an 87% hydrolyzed poly(vinyl acetate), (2) poly(vinyl alcohol) (PVA) (Fluka) with a 40% hydrolyzed poly(vinyl acetate) all prepared in our laboratory, and (3) poly(vinyl acetate) (Aldrich). Water was prepared with a Milli-Q Plus water purification system (Millipore). Methanol and glutaraldehyde was purchased from Fluka Company. All other solvents and chemicals were of analytical grade.

2.2. Preparation of neem Aza-A solution

Neem seed kernels (5 g) had their cortex removed then crushed into small pieces, deoiled by grinding in light petroleum (200 mL) and filtered. The grinding and filtering were repeated twice more. The deoiled neem seed powder was stirred in 200 mL of methanol for 2 h and filtered at room temperature. The meal was reextrated with two further portions of methanol. The combined methanol filtrates were concentrated to approximately 50 mL, the aqueous methanol solution was extracted three times with an equal volume of n-hexane (each was 50 mL) followed by 3 mL × 50 mL of dichloromethane (Fluka Company). The methanol–water layer was discarded and the dichlormethane layers were combined and dried over $MgSO_4$ (Fluka Company) and then evaporated to dryness. Two grams of the product were dissolved in 8 mL of hexane during stirring. The liquid was separated into two layers using a separating funnel. The process was repeated by addition of a further 8 mL of ether. The methanol layer was evaporated and the residue was dissolved in 2 mL dichloromethane and then treated with 10 mL n-hexane and 10 mL ether, according to the above-mentioned process. The final yield of 65.0% Aza-A was 0.8 g from 1 kg of neem seeds.

2.3. Capsules preparation

The ratios of polymer with 0, 40 and 87% hydrolyzed poly(vinyl acetate) to distilled water containing glutaraldehyde 5% (w/v) and 0.1% hydrochloric acid, are shown in Table 1, were prepared for the encapsulation of the neem Aza-A product. Suitable amounts of the neem Aza-A product in solution were added to the polymer solutions in water to obtain mixtures of the neem Aza-A solution:polymer in the proportion of 10:5 (w/w). Microcapsules were obtained by spraying the solutions through a mini Buchi-191 spray dryer equipped with a 0.7 mm nozzle at 206 kPa. The microparticles were collected and stored under vacuum at room temperature for 48 h.

2.4. Measurement of diameter

The diameters of beads were measured using an optical microscope (OM, and scanning electron microscope (SEM), JMS-5800 LV, JEOL). The capsule particles were collected at the outlet of the channel without being assembled. Average diameters were calculated over samples of at least 40 bead particles.

2.5. Swelling study

Capsule samples were weighed and immersed in Millipore water for a period of over 35 h at 32 °C. The samples were then dried in an oven at 50 °C for 24 h and weighed until a constant weight was achieved. The degree of swelling ratio was estimated from this Eq. (1)

$$\text{Swelling ratio} = \frac{W_2 - W_1}{W_1} \quad (1)$$

where W_1 = the original weight of the sample; W_2 = the weight of swollen sample. This experiment was repeated three times.

2.6. Irradiation experiments

Solutions of neem Aza-A extract in methanol were applied to the surface of glass slides using a pipette and the methanol was evaporated at room temperature, leaving the slide with a thin layer of neem Aza-A. These slides were exposed to UV light under a UV lamp (UV B CLEO 15W, T.S.T. Supplies & Trading Co., Ltd.) (254 nm, at a distance of 10 cm). At intervals, two slides were removed and rinsed with methanol (total 2 mL) and then analyzed for neem Aza-A using HPLC (Bio-Rad Laboratories). The total period of the test was 44 h. The irradiation experiment was repeated three times.

2.7. Recovery of neem Aza-A

Solutions (50 μL) containing 206 μg of neem Aza-A extract without UV light absorbers in methanol were applied onto the surface of glass slides. After the methanol was evaporated, slides were rinsed with 2 mL of methanol. The residual neem Aza-A was estimated by HPLC (Bio-Rad Laboratories) and this experiment was repeated three times.

2.8. Encapsulation yield (EY)

The EY was calculated as the ratio of the mass of the microcapsules obtained at the end of the process and the mass of the initial substances added including neem Aza-A.

2.9. Encapsulation efficiency (EE)

The EE was calculated as the ratio between the initial mass of neem Aza-A used for encapsulation and its mass in the final product. About 20 mg of exactly weighed microcapsule sample was extracted in distilled water to form a homogeneous solution. The total neem Aza-A in the solution was extracted for 48 h with a 50/50 MeOH/H_2O mixture and its mass was determined by HPLC (Bio-Rad Laboratories).

Table 1
Particle size, efficiency of yield and efficiency of encapsulation obtained at different ratios between polymer and distilled water containing glutaraldehyde 5% (w/v) and 0.1% hydrochloric acid.

Ratio between polymer and distilled water	Average particle size (μm) (±S.D.) observed by OM	Average particle size (μm) (±%S.D.) observed by SEM	%Efficiency of yield (±%S.D.)	%Efficiency of encapsulation (±%S.D.)
0% hydrolyzed poly(vinyl acetate)				
1:20	15(2)	11(3)	85(2)	75(4)
1:35	14(3)	9(3)	95(2)	78(4)
1:40	14(2)	8(2)	96(2)	79(2)
40% hydrolyzed poly(vinyl acetate)				
1:20	15(2)	10(2)	86(3)	76(2)
1:35	14(3)	9(3)	94(2)	78(2)
1:40	15(2)	8(2)	96(3)	80(3)
87% hydrolyzed poly(vinyl acetate)				
1:20	16(4)	12(3)	84(4)	79(3)
1:35	14(2)	8(3)	96(2)	80(5)
1:40	15(3)	9(3)	97(2)	81(2)

2.10. Release of neem Aza-A from capsules

Approximately 8% of the capsule mass containing the neem Aza-A product were used. The release study was performed in distilled water. An 8 mg sample of the capsule was dispersed in 500 mL of the release water medium at 25 °C. The supernatant was collected after certain time intervals to determine the amount of the neem Aza-A product released, as determined by HPLC (Bio-Rad Laboratories). This experiment was repeated three times.

2.11. Infrared spectroscopy (IR) and X-ray diffraction

IR was performed on the hydrolyzed poly(vinyl acetate) with 0, 40 and 87% hydrolyzed poly(vinyl acetate), in the range of 400–4000 cm^{-1}, using KBr pellets in a Shimadzu FTIR-8300 spectrometer.

The crystallinity of the polymer matrix was observed by X-ray diffractometry performed on a X' Pert MPD, Philips X-ray diffractometer under the following conditions: nickel filtered CuKα radiation (λ = 0.15406 nm) at a current of 25 mA and a voltage of 35 kV. The scanning rate was 4 °/min in the angle range of 8–80° (2θ).

3. Results and discussion

3.1. FTIR and XRD study

Results of the FITR analysis of the 0, 40, 87% hydrolyzed poly(vinyl acetate) are shown in Fig. 1. The broad OH peak of the 40% hydrolyzed poly(vinyl acetate) was small compared to that of the 87% hydrolyzed poly(vinyl acetate), and the intensity of the carbonyl peak was much higher and comparable to that in the non-hydrolyzed poly(vinyl acetate). Thus, the higher intensity peaks in the 40% hydrolyzed poly(vinyl acetate) were comparable to the non-hydrolyzed poly(vinyl acetate), while the low intensity peaks are comparable to those in the 87% hydrolyzed poly(vinyl acetate).

The diffraction pattern of capsules having 0% hydrolyzed poly(vinyl acetate) (Fig. 2) shows two peaks, one of high intensity at 19.8° which corresponds to (1 1 0) reflection [21] and one of low intensity at 39.7° resulting from the crystalline phase. Also, there is a broad region under these peaks ranging from roughly 5 to 80° that is related to the predominant amorphous phase. The diffraction patterns of capsules from the 40 or 87% hydrolyzed poly(vinyl acetate) exhibited two major peaks characteristic of a crystalline polymer at 19.45° (strong), and 40.89° (weak). The capsule with 87% hydrolysed poly(vinyl acetate) had the highest crystalline region compared to the other samples due to its microstructure with a low amount of vinyl acetate. A broad peak centered at 2θ = 19.51° can be associated with the amorphous behaviour of pure PVA. This peak corresponds to (1 1 0) reflection. All the diffraction patterns included three peaks, at 2θ = 11.49°, 17.48°, and 41.34° that corresponded to the crystalline phase of PVA [14].

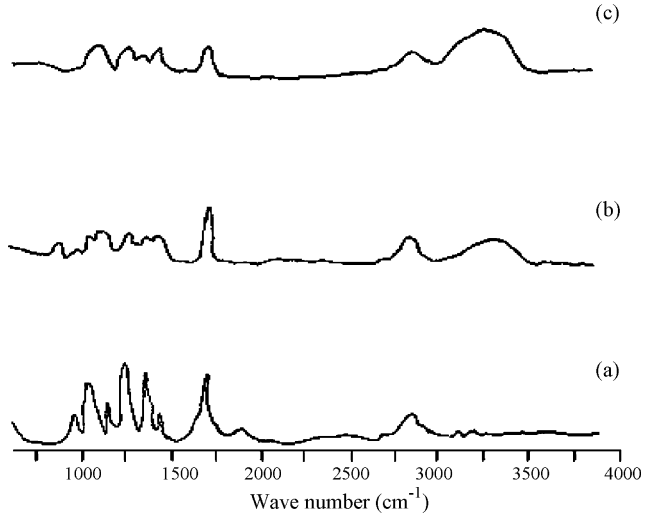

Fig. 1. Spectra of (a) 0, (b) 40, and (c) 87% hydrolyzed poly(vinyl acetate) observed by FTIR.

3.2. Morphology of microcapsule, encapsulation yield and encapsulation efficiency

The particle size of the capsule beads was analyzed using both an optical microscope (OM) and SEM as shown in Table 1. Fig. 3

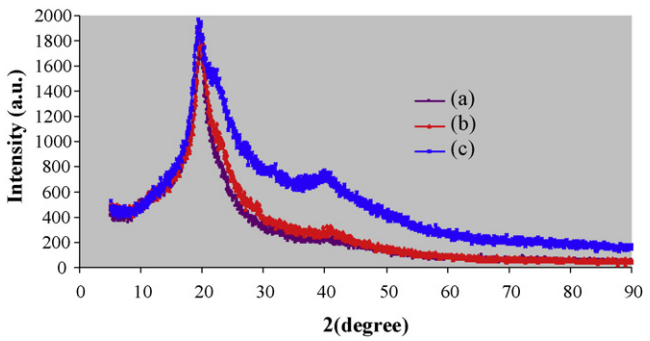

Fig. 2. X-ray diffraction patterns of (a) 0, (b) 40, and (c) 87% hydrolyzed poly(vinyl acetate) films.

illustrates OM micrographs of capsules obtained from (a) 0, (b) 40 and (c) 87% hydrolysed poly(vinyl acetate). It is obvious that the morphology of capsules show little change and overall the average particle size of the capsules was 12 μm.

The SEM photomicrographs of the microcapsules are shown in Fig. 4. The average diameter of capsules obtained from the 0, 40 and 87% hydrolysates of poly(vinyl acetate) were 10, 9 and 8 μm at a ratio between polymer and distilled water, 1:35, respectively. Some aggregates of capsules obtained from three types were observed. The particle sizes of capsule observed from OM were larger than that of capsule analyzed from SEM due to shrinkage of the capsule after SEM sample preparation.

The ratio between water and polymer, and percentage hydrolyzed poly(vinyl acetate) on encapsulation yield (EY), and encapsulation efficiency (EE) were investigated (Table 1). When the ratios of water and non-hydrolyzed poly(vinyl acetate) decreased from 1/20, 1/35 and 1/40, the encapsulation yields were about 85, 95 and 96%, respectively. In the case of the encapsulation efficiency, the result showed similar trends to the efficiency yield. The encapsulation efficiency of capsules was 75, 78, and 79 when the ratio between non-hydrolyzed poly(vinyl acetate) and distilled water was 75, 78, and 79%, respectively. When the degree of percentage hydrolyzed poly(vinyl acetate) was increased from 0 to 40%, the efficiency yield was 86, 94, and 96% at 1/20, 1/35 and 1/40 (40% hydrolyzed poly(vinyl acetate)/distilled water), respectively, whereas the encapsulation efficiency of this system was 76, 78, and 80% when the ratio of 40% hydrolyzed poly(vinyl acetate)/water were 1/20, 1/35 and 1/40, respectively. In the case of the 87% hydrolyzed poly(vinyl acetate), the efficiency yield was 84, 96, and 97 when the ratios between 87% hydrolyzed poly(vinyl acetate) and distilled water were 1/20, 1/35, and 1/40, respectively. The encapsulation efficiency of this system was 79, 80 and 81 when the ratios of 87% hydrolyzed poly(vinyl acetate) and distilled water were 1/20, 1/35, and 1/40, respectively.

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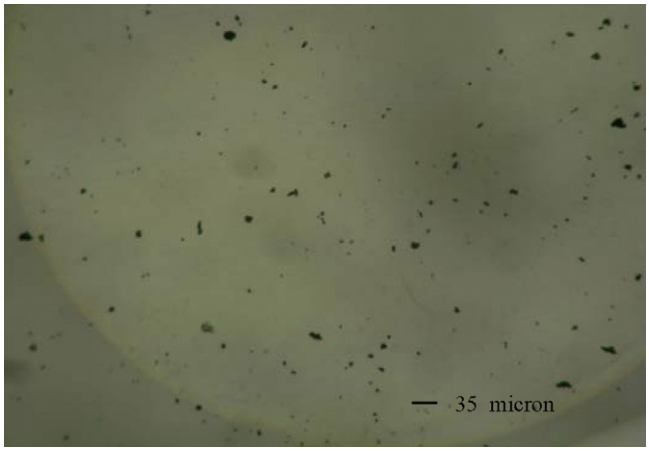

Fig. 3. Optical micrography of microcapsule with 87% hydrolyzed poly(vinyl acetate).

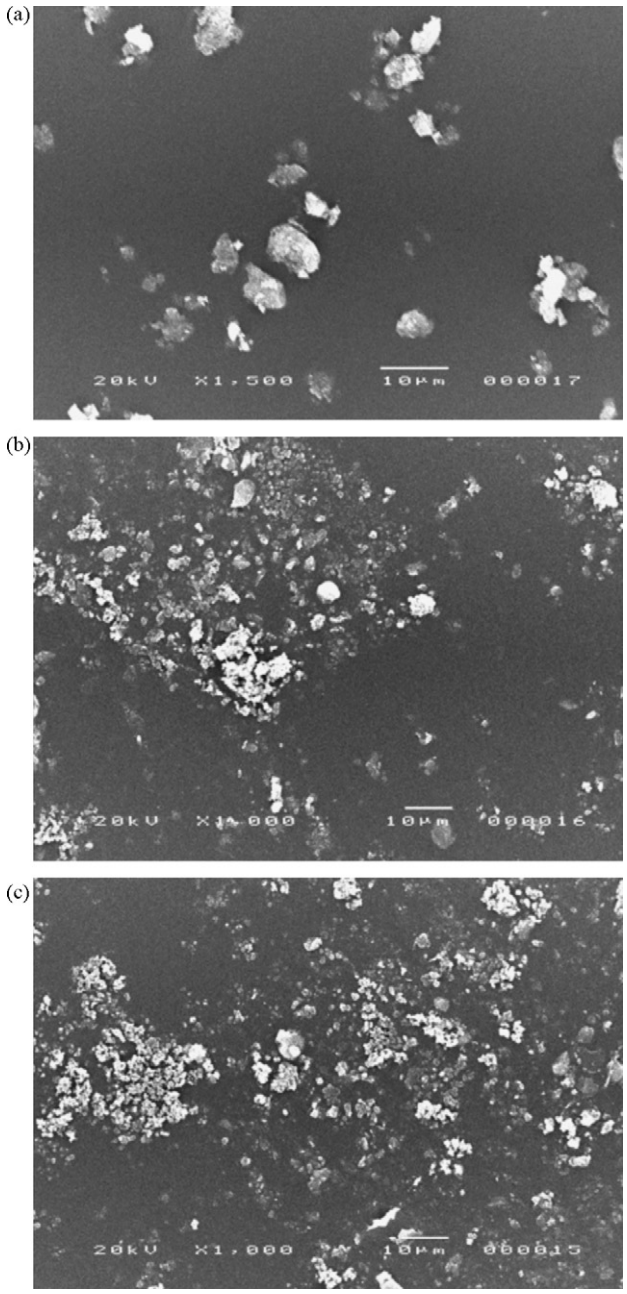

Fig. 4. SEM micrographs of capsules obtained from a PVA:distilled water ratio of (1:35) and a percentage hydrolysis of poly(vinyl acetate) of (a) 0, (b) 40, and (c) 87%.

(40% hydrolyzed poly(vinyl acetate)/distilled water), respectively, whereas the encapsulation efficiency of this system was 76, 78, and 80% when the ratio of 40% hydrolyzed poly(vinyl acetate)/water were 1/20, 1/35 and 1/40, respectively. In the case of the 87% hydrolyzed poly(vinyl acetate), the efficiency yield was 84, 96, and 97 when ratios between 87% hydrolyzed poly(vinyl acetate) and distilled water were 1/20, 1/35, and 1/40, respectively. The encapsulation efficiency of this system was 79, 80 and 81 when the ratios of 87% hydrolyzed poly(vinyl acetate) and distilled water were 1/20, 1/35, and 1/40, respectively.

3.3. Swelling study

The swelling of any capsule in a solvent depends upon the diffusion coefficient of the solvent, the relaxation rate of the amorphous regions of the polymer chain and its degree of crystallinity

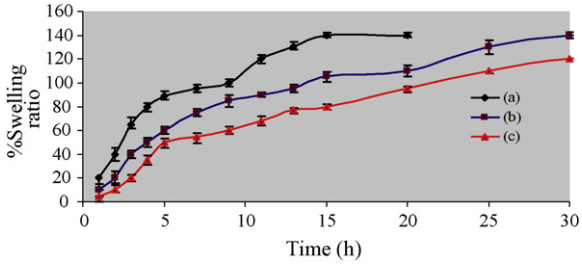

Fig. 5. Swelling ratio of capsule with (a) 0, (b) 40, and (c) 87% hydrolyzed poly(vinyl acetate).

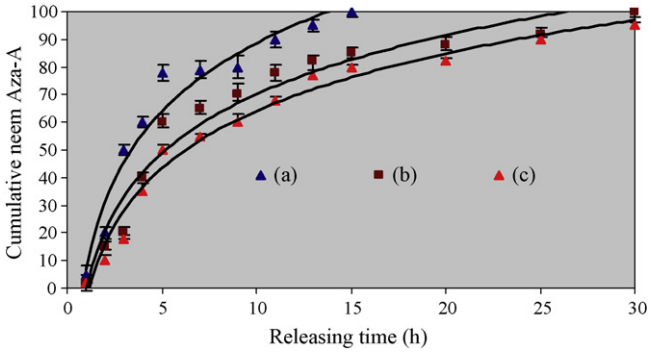

Fig. 7. Relationship between the release rate of neem Aza-A and the release time from microcapsules obtained from (a) 0 hydrolyzed poly(vinyl acetate), (b) 40 hydrolyzed poly(vinyl acetate), and (c) 87% hydrolyzed poly(vinyl acetate).

and crosslinking density in the polymer matrix. Fig. 5 depicts the swelling ratio of neem Aza-A capsules prepared from different percentage hydrolyzates of poly(vinyl acetate) and crosslinking densities in a water medium and storage time over 35 h. It is clear that the swelling ratio of capsules obtained from the 0% hydrolysed poly(vinyl acetate) was lower than that capsule having 40 and 87% hydrolyzed poly(vinyl acetate) due to lower crosslinking density occurring from the hydroxyl groups in polymer and glutaraldehyde and the lower crystallinity in the sample observed from XRD.

3.4. Release of neem Aza-A from the capsule

The neem Aza-A was dispersed evenly throughout the matrix of the capsule and was unable to diffuse to any significant extent within the matrix. However when the polymer matrix was placed in a thermodynamically compatible medium, the hydrolyzed poly(vinyl acetate) swelled owing to absorption of the medium, then the neem Aza-A in the swollen part diffused out of the polymer matrix. The release of the neem Aza-A from the polymer matrix has been schematically described in Fig. 6. In hydrophilic membranes, there are usually both geometric and mechanical reactions with respect to swelling [19]. At the same time, there are cases where the polymer matrix exhibits swelling with no significant limitations. The variety of factors affecting the rate of the diffusion transfer of a solvent, including (a) the polymer transition from glassy to rubber-like state; (b) relaxation transitions on the surface and in the bulk of a sample; (c) dependence of the diffusion mobility of water on its concentration in the polymer; (d) expansion of the sample, reaching several tens or even a few hundreds percentages with respect to the initial dimensions, requires development of a complicated multiparametric model of the water transport in polymers.

Results of a study of the effect of the neem Aza-A concentration on its rate of release in distilled water from capsules with 0, 40 and 87% hydrolyzed poly(vinyl acetate) is shown in Fig. 7. It is clear that the release rate of neem Aza-A from the microcapsules was proportional to the release time. The release rate of neem Aza-A from microcapsules obtained from the non-hydrolyzed poly(vinyl acetate) was high during the first 10 h followed by a slow release. Release of neem Aza-A from the non-hydrolyzed poly(vinyl acetate) microcapsules was found to be almost complete within about 15 h.

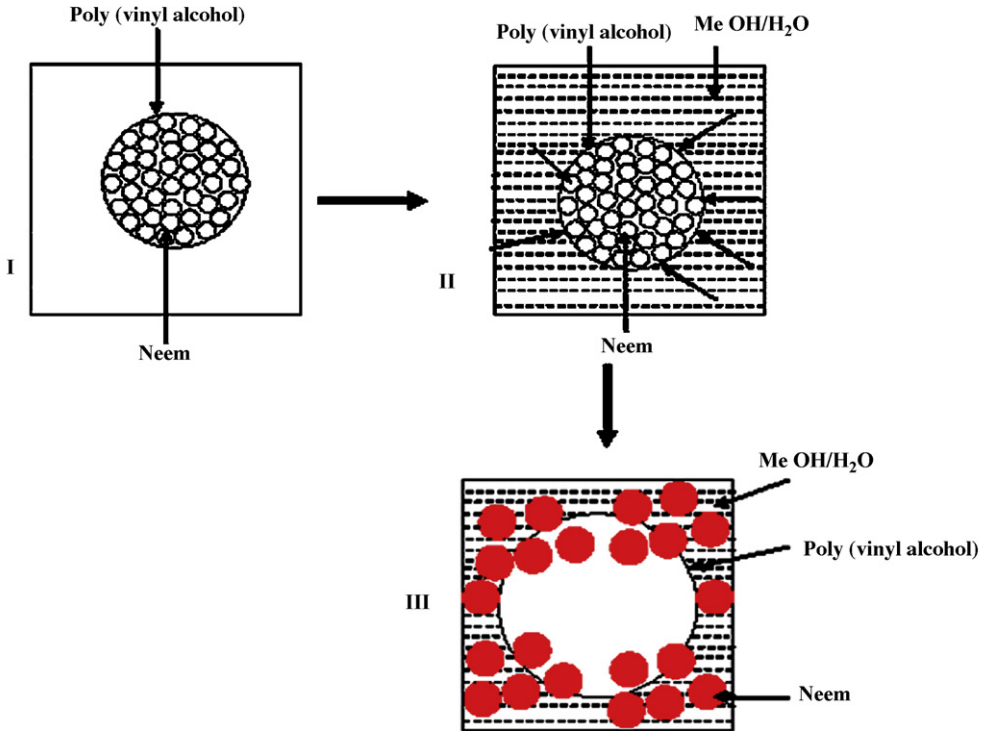

Fig. 6. Schematic representation of a possible swelling type controlled release system of neem containing Aza-A (I) neem Aza-A entrapped in poly(vinyl alcohol), (II) neem containing Aza-A entrapped in poly(vinyl alcohol) in a thermodynamically stable system with H_2O diffusing into the polymer matrix, and (III) neem Aza-A released into the H_2O system on swelling of the polymer matrix.

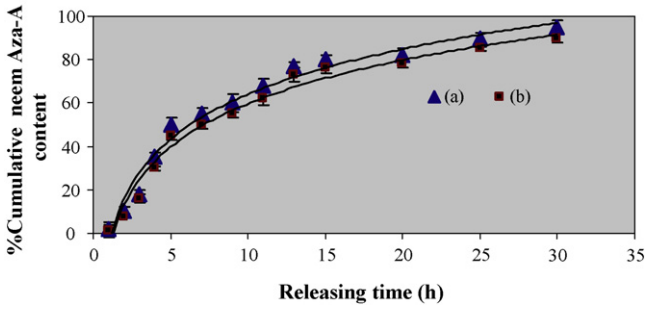

Fig. 8. Relationship between the release rate of neem Aza-A and release time from microcapsules obtained from 87% hydrolyzed poly(vinyl acetate) having diameters of (a) 8 and (b) 12 μm.

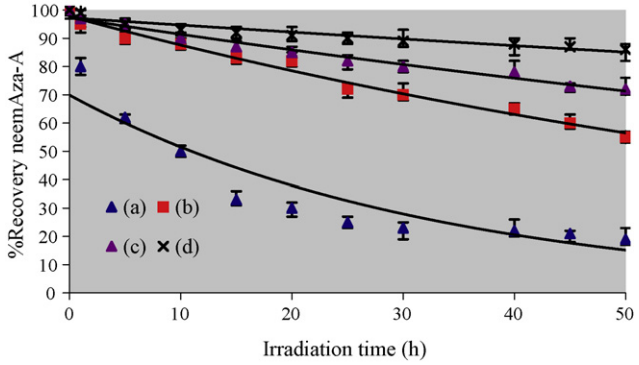

Fig. 9. Recovery of neem Aza-A after UV irradiation of (a) unencapsulated neem Aza-A, and encapsulated neem Aza-A in (b) 0 hydrolyzed poly(vinyl acetate), (c) 40 hydrolyzed poly(vinyl acetate), and (d) 87% hydrolyzed poly(vinyl acetate).

This result indicates that high amounts of neem Aza-A was present on the surface of the capsules. In the case of capsules obtained from the 40 and 87% hydrolyzed poly(vinyl acetate), the release rate of neem Aza-A from the microcapsules was high during the first 15 h followed by a slow release. Finally, release of neem Aza-A from the microcapsules obtained from 40 and 87% hydrolyzed poly(vinyl acetate) was found to be almost complete within about 25 and 30 h, respectively. This result indicates that neem Aza-A was entrapped in the polymer matrix crosslinked with glutaraldehyde. This could be explained by the amount of neem Aza-A released being dependent on its hydrophilicity and crosslinking density in the polymer matrix.

The effect of the particle size of the capsule on releasing neem Aza-A from the capsule in aqueous medium is depicted in Fig. 8. It is clear that the percent cumulative neem Aza-A of the capsule with 8 μm diameter was higher than that of sample having a 12 μm diameter due to the higher surface area, leading to a greater amount of neem Aza-A diffusing in the aqueous phase.

3.5. Photodegradation of unencapsulated and encapsulated neem Aza-A

The stability of neem Aza-A subjected to UV irradiation is reported in terms of the percentage residual neem Aza-A (Fig. 9). It was found that the rate of degradation of unencapsulated neem Aza-A was much swifter than that of the encapsulated neem Aza-A. The rate of neem Aza-A degradation reduced rapidly from the time of initiation and became constant after 30 h of UV irradiation. When the neem oil was irradiated for 10 and 30 h, the residual neem Aza-A was 50 and 19%, respectively. This result correspond to those from the work of Sundaram and Curry [20]. They studied the photostabilization of neem-based azadirachtin insecticide (AZ-A) applied onto a glass surface in the presence of three UV absorbers, 2,4-dihydroxybenzophenone (Uvinul M-41)0, UM), 4-aminobenzoic acid (PABA) and Fluorescent brightener-28 (FB-28), a stilbene disulfonic acid derivative. It was found that for effective photostabilization, both AZ-A and the UV absorber must have matching UV spectra with a similar λ_{max}. The mechanism of photostabilization was likely due to either energy transfer from AZ-A to the UV absorber and/or competitive absorption of UV photons by the absorber. Photoinstability of AZ-A in the presence of FB-28 was due to energy transfer from the activated FB-28 to AZ-A molecules. Based on the UV spectral data, UV protectants can be selected and matched to stabilize UV-labile pesticides.

The employed material matrix for encapsulation of neem Aza-A was 0, 40, and 87% hydrolyzed poly(vinyl acetate). These results show that the efficiency of thermal stability for encapsulated neem Aza-A obtained from the 87% hydrolyzed poly(vinyl acetate) was higher than that of other samples. The residual neem Aza-A for encapsulated neem Aza-A obtained from the non-hydrolyzed poly(vinyl acetate) was 85 and 78% after 10 and 30 h of UV irradiation time. In the case of 40% hydrolyzed poly(vinyl acetate), the residual neem Aza-A was 88 and 82% after 10 and 30 h of UV irradiation time, respectively. When the degree of hydrolysis of poly(vinyl acetate) was increased from 40 to 87% and 90%, the residual neem Aza-A was 95 and 90% after 10 and 30 h of UV irradiation time respectively.

The rate constant values for photodegradation (h^{-1}) are given in Table 2. The photodegradation of unencapsulated or encapsulated neem Aza-A under ultraviolet irradiation were investigated. The rate constant values of unencapsulated neem Aza-A under ultraviolet irradiation were found to be higher than that of encapsulated neem Aza-A. The rate constants of unencapsulated and encapsulated neem Aza-A derived for the non-hydrolyzed poly(vinyl acetate) were 0.014616 and 0.014616 h^{-1}, respectively. When the percentage of hydrolyzed poly(vinyl acetate) was increased from 0 to be 40 or 87%, the rate constants for the encapsulated neem Aza-A were found to be 0.005447, and 0.002782 h^{-1}, respectively. This confirms that the neem Aza-A was entrapped and partially protected within the hydrolyzed poly(vinyl acetate) matrix.

The aim of this part of the investigation was to compare the efficiency of photodegradation between the encapsulated and unencapsulated neem Aza-A. This estimation was based on defining the efficiency of the photodegradation data, as the irradiation time (in hour units) needed to reduce the amount of neem Aza-A to 30% of the initial value under accelerated conditions is given in Table 3.

Table 2
Rate constant values of unencapsulated or encapsulated neem Aza-A for photodegradation.

Sample name	Rate constant value of unencapsulated or encapsulated neem Aza-A for photodegradation (k, h^{-1})
Unencasulated neem Aza-A	0.014616
Encapsulated neem Aza-A Obtained from percent hydrolyzed poly(vinyl acetate)	
0	0.008287
40	0.005447
87	0.002782

Table 3
Efficiency of photodegradation of encapsulated and unencapsulated neem Aza-A under accelerating condition.

Sample name	Efficiency of photodegradation[a] (h)
Unencasulated neem Aza-A	3
Encapsulated neem Aza-A Obtained from percent hydrolyzed poly(vinyl acetate)	
0	30
40	50
87	>50

[a] Efficiency of photodegradation means the irradiation time (in h units) needed to reduce the amount of neem Aza-A to 30% of its initial value.

It is clear that the efficiency of photodegradation of unencapsulated neem Aza-A was 3 h. In the case of encapsulated neem Aza-A, it was found that the efficiency of photodegradation of encapsulated neem Aza-A was lower than that of unencapsulated neem Aza-A. The photodegradation of encapsulated neem Aza-A obtained from 0 and 40% hydrolyzed poly(vinyl acetate) was 30 and 50 h, respectively. When the degree of hydrolyze poly(vinyl acetate) was increased from 40 to 87%, the photodegradation of encapsulated neem Aza-A was above 50 h. This indicates that the encapsulated neem Aza-A helped to improve its stability to photodegradation.

4. Conclusions

The encapsulation of neem Aza-A was successfully carried out for the first time in 0, 40 and 87% hydrolyzed poly(vinyl acetate) capsules, that produced a slow release of neem Aza-A that is suitable for application in the agricultural industry. It can be concluded that neem Aza-A is highly photolabile in the presence of UV light. The encapsulation did improve the stability of neem Aza-A under conditions that facilitated photodegradation. The swelling of the capsules decreased with the increasing degree of hydrolysis of the glutaraldehyde crosslinked vinyl acetate. The capsules obtained from the 87% hydrolyzed poly(vinyl acetate) gave the highest photodegradative stability of neem Aza-A. Therefore, this method can be used to enhance the storage of neem Aza-A under conditions that allow for photodegradation. In the present study, the use of hydrolyzed poly(vinyl acetate) for the controlled release of neem Aza-A results in increased photodegradation stability with an extended shelf life of the neem Aza-A.

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